



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

0 095 919
A2

12

EUROPEAN PATENT APPLICATION

21 Application number: 83303089.3

51 Int. Cl.³: C 08 L 25/12, C 08 L 33/08

22 Date of filing: 27.05.83

30 Priority: 01.06.82 IT 2161982

71 Applicant: Montedison S.p.A., 31, Foro Buonaparte,
I-20121 Milan (IT)

43 Date of publication of application: 07.12.83
Bulletin 83/49

72 Inventor: Fiore, Leonardo, 46, Via de Lemene, Milano (IT)
Inventor: Binaghi, Marco, 43, Via Sismondi, Milano (IT)
Inventor: Bonicelli, Ugo, 6, Via Cavezzali, Milano (IT)

54 Designated Contracting States: DE FR GB NL

74 Representative: Whalley, Kevin et al, Marks &
Clerk 57/60 Lincoln's Inn Fields, London WC2A 3LS (GB)

52 Process for the preparation of mixes or blends of acrylic rubbers with styrene/acrylonitrile copolymers.

57 The impact-resistance characteristics of styrene/acrylonitrile copolymers (SAN) are improved by the admixture to them of acrylic rubbers consisting of either copolymers or terpolymers of ethyl and/or butyl acrylate with acrylic and/or methacrylic acid, by carrying out the mixing in the presence of from 0.05 to 2% by weight of ZnCl₂, CdCl₂, FeCl₃, AlCl₃, or BF₃·(C₂H₅)₂O, and of 0.5-5 mols, based on 100 mols of acrylic rubber, of an epoxy cross-linking compound, at a temperature comprised between the glass transition temperature of the SAN copolymer and 220°C.

EP 0 095 919 A2

"PROCESS FOR THE PREPARATION OF MIXES OR BLENDS OF
ACRYLIC RUBBERS WITH STYRENE/ACRYLONITRILE
COPOLYMERS"

The present invention relates to a process for the preparation of mixes or blends of acrylic rubbers with styrene/acrylonitrile copolymers, having improved impact-resistance characteristics.

5 It is known that an improvement of the impact resistance properties of a relatively fragile (brittle) thermoplastic material such as a styrene/acrylonitrile copolymer (SAN) may be obtained by the addition to the SAN of a gummy polymer with a sufficiently high degree
10 of chemical/physical compatibility with the SAN.

Usually the compatibility of the rubber with the SAN is achieved by grafting onto the rubber segments of styrene/acrylonitrile copolymer. The rubbers used for such a grafting may be of different types. Those
15 normally used are polybutadiene, ethyl- and/or butyl polyacrylate, and the ethylene/propylene/diene terpolymers. The grafting onto the rubber may be carried out

- 2 -

in various different ways. Thus, for instance, the rubber may be treated in an emulsion or suspension or in solution, by the addition of a radical catalyst and of a mix or blend of styrene and acrylonitrile monomers.

5 In any case, the modification of the rubber requires special circumstances in which to start the grafting. The grafted rubber must then undergo separation from the residual monomers, purification and drying before it may be admixed with the SAN in the desired ratio.

10 The rigid SAN matrix is in general synthesized separately. In some instances the matrix may be prepared in the same reactor in which is carried out the grafting of the rubber. In this case the process is, however, made even more complicated by the higher number of
15 variables to be controlled.

It has now been found by the present Applicants that it is possible to make particular types of acrylic rubber compatible with SAN, that is to obtain an improvement of the impact-resistance characteristics of
20 the SAN by the addition of the acrylic rubber, carrying out the mixing together of the two products in the presence of particular compounds of the Lewis acid type.

Thus, the present invention provides a process for the preparation of a blend or mix of an acrylic rubber
25 which comprises a copolymer of ethylacrylate and/or

- 3 -

butylacrylate with acrylic and/or methacrylic acid with a styrene/acrylonitrile copolymer, which process comprises mixing together the acrylic rubber with the acrylonitrile/styrene copolymer, at a temperature from 5 the glass transition temperature of the acrylonitrile/styrene copolymer to 220°C, in the presence of from 0.05 to 2% by weight, based on the weight of the polymeric mixture, of a compound selected from zinc chloride, cadmium chloride, ferric chloride, aluminium chloride, 10 and boron trifluoride, and in the presence of an epoxidic cross-linking agent.

It is thus possible to eliminate the whole of the preparatory stage of the grafted rubber and to conduct the reaction on the conventional standard machines used 15 for the mixing of the SAN with the rubber, and for the successive operation, with an evident economical advantage, derived from the lower investment required for the equipment and for the simplification of the operations of the process. The use of acrylic rubber 20 in the blend also imparts to it advantageous weather-proof characteristics, due to unsaturation in the gummy stage. Such unsaturation, present in other rubbers, in fact represents a preferential point of attack for the thermo- and photo-oxidation reactions.

25 The Lewis acid used is a halide of the type : ZnCl_2 , CdCl_2 , FeCl_3 , AlCl_3 , $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$; $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ is the chemical form in which boron trifluoride is generally used. S u c h h a l i d e

- 4 -

is used in an amount from 0.05% to 2% by weight based on the total weight of the polymeric blend.

Zinc chloride is preferred, more preferably in an amount of from 0.1% to 1% based on the mix or blend.

5 The acrylic rubber must possess particular characteristics of cross-linking, such that it will be possible to achieve with a single catalyst and in a single operation the grafting and cross-linking reactions.

10 Typical examples of suitable rubbers are either copolymers consisting of 95-99.5 mol per cent of an ethyl- or butyl-acrylate and 5-0.5 mol per cent of an acrylic and/or methacrylic acid, or terpolymers of 95-99.5 mol per cent of a mixture of ethyl- and butyl-
15 -acrylate and 5-0.5 mol per cent of acrylic and/or methacrylic acid. Such copolymers or terpolymers must be used in the presence of a cross-linking agent of the epoxy type, that may be used in a mixture or in the form of a product chemically bound to the chain of the macro-
20 molecule of the copolymer or terpolymer. Such an epoxidic agent must have at least two epoxy functions when used in admixture with acrylic rubber, while it may, but not necessarily, be mono-functional when present as a product chemically bound to the rubber.

25 Preferably, the epoxy agent or compound is used in an amount from 0.5 to 5 mols based on 100 mols of

- 5 -

acrylic rubber, or, in the case that it is chemically bound to the rubber, on 100 mols of the total of monomeric units consisting of ethyl and/or butyl acrylate and acrylic and/or methacrylic acid.

5 Examples of such epoxy-compounds that may be used in admixture with acrylic rubber are diglycidylether of bisphenol A, ethyleneglycol-diglycidylether, and in general all the diepoxy and polyepoxy compounds, and all the epoxy resins having such a molecular weight as
10 to be compatible or miscible with acrylic rubber. As epoxidic cross-linking agents chemically bound to the macromolecule of acrylic rubber, there may be mentioned as an example the glycidylether acrylates.

 The blend of acrylic rubber with the SAN may be
15 carried out at a temperature from the glass transition temperature of the SAN (about 140°C) to about 220°C. In practice the operating temperature is from 160°C to 220°C.

 The quantity of acrylic rubber to be admixed with
20 the SAN in the process of the present invention may vary within a wide range, for example from 5% to 50%, more preferably from 10% to 30%, by weight based on the weight of the blend with the SAN, depending on the degree of reinforcement desired.

25 The SAN used is preferably formed from 25-35 mol

- 6 -

per cent of acrylonitrile and 75-65 mol per cent of styrene.

The blending or mixing may be carried out on conventional (standard) equipment for the processing of polymers, such as a Banbury mill, extruder, or cylinder mixer. The operational conditions vary with the type of machine used.

The increase in impact-resistance of the blend made according to the present invention, with respect and in comparison to the impact-resistance of a simple mechanical blend, is considerable and may even attain 400%.

The invention will be further described with reference to the following illustrative Examples.

15 In the evaluation of the impact-resistance characteristics of the materials obtained according to the procedures described in the examples that follow, there was used the ASTM D 256 Method B Test (Charpy test) on test pieces or specimens 1/8 inch thick and 20 with a notch or indent, obtained by a mechanical process from small plates of the same thickness, obtained by compression moulding.

The elasticity coefficient or modulus under bending was determined through a "bounce-test" on specimens 25 identical with those subjected to the Charpy test, but

- 7 -

without a notch. The measurement was carried out on a pendulum instrumented for Charpy-tests, with an impact velocity of 10 cm/sec. The flexural modulus or coefficient was calculated from the time of contact of the testing hammer with the specimen, through the formula :

$$E = \frac{\pi^2}{t^2} \frac{Ml^3}{48 I}$$

where E = elasticity modulus
 t^2 = time of contact
 10 M = effective mass of hammer
 I = moment of inertia
 l = distance between the supports of the specimen.

The characteristics of the SAN used in the following examples are given in Table 1 below.

(The trade names KOSTIL AF, KOSTIL AM and KOSTIL AP refer to styrene/acrylonitrile copolymers produced by MONTEDISON S.p.A.).

T A B L E 1

Name of product	Content of acrylonitrile (mol%)	Intrinsic viscosity in Tetrahydrofuran at 30°C ml/g)	Mean numerical molecular weight
KOSTIL AF	28	84	70,000
KOSTIL AM	25	78	62,000
KOSTIL AP	27	65	53,000

The characteristics of the acrylic rubbers (Elaprim AR 152 and AR 153) used in the following examples are given below.

(The trade names Elaprim AR 153 and Elaprim AR 152
5 refer to acrylic rubbers produced by MONTEDISON S.p.A).

ELAPRIM AR 153: blend formed of 100 parts by weight of
copolymer of ethylacrylate (99% by
weight) and acrylic acid (1% by weight),
10 with 3 parts by weight of diglycidyl-
ether of bisphenol A. This mix or
blend has a Mooney viscosity at 100°C
of 48.

ELAPRIM AR 152: blend formed of 100 parts by weight of
15 terpolymer of ethylacrylate (64% by
weight)/butylacrylate (35% by weight)
and acrylic acid (1% by weight), with
3 parts by weight of diglycidylether
of bisphenol A. This blend has a
Mooney viscosity at 100°C of 37.

20 EXAMPLE 1

15 Grams of Elaprim AR 153 rubber and 35 g of SAN co-
polymer (Kostil AP) were mixed together in a Brabender
mill running at 100 r.p.m. and having the mixer barrel
pre-heated by oil circulation at 170°C.

25 After 2 minutes there were added 0.15 grams of anhydrous
zinc chloride, and mixing was then continued for a
further 10 minutes. At the end of the mixing, the
temperature of the mix or blend was about 220°C. The

- 9 -

polymeric mass was thereupon extracted from the mixing mill and compression moulded.

A portion of the blend was then finely comminuted and extracted in an extractor with boiling acetone, in
5 order to separate the gummy part of the SAN that had not reacted. Elementary analysis of the part insoluble in acetone showed a content in nitrogen of 1.1%, corresponding to a percentage of acrylonitrile bound to the rubber of about 4.1%.

10 EXAMPLE 2 (for comparative purposes):

The same procedure was followed as in Example 1, but omitting the addition of the zinc chloride. The end or final temperature of the blend was about 200°C.

EXAMPLE 3 (for comparative purposes):

15 The same procedure was followed as in Example 1, but using instead of Elaprim AR 153 rubber, an ethyl acrylate/acrylic acid copolymer containing 1 mol per cent of acrylic acid (thus operating in the absence of cross-linking epoxy).

20 EXAMPLE 4

The procedure according to Example 3 was repeated, but there was added to the blend 0.45 grams of diglycidyl-ether of bisphenol A.

In Table 2 below are given the Charpy resilience

coefficients and the elasticity modulus under bending of the products obtained in Examples 1 to 4.

T A B L E 2

5	Example	Charpy resilience (kg.cm/cm ²)	Elasticity modulus under bending (kg/cm ²)
	1	14.66	19,500
	2	6.6	18,900
	3	6.8	19,600
	4	17.5	19,700

EXAMPLE 5

Into a Banbury mill of 1300 cc holding capacity, there were introduced 910 grams of Kostil AP and 390 g of Elaprim AR 153. After mixing for 5 minutes, to the mix
15 were added 4 g of anhydrous zinc chloride. Thereupon, mixing was continued at 210°C for 10 minutes, after which the molten mass was discharged from the Banbury mill and allowed to cool down, after which it was ground in a mill. From the ground material there were
20 obtained by compression moulding test pieces or specimens to be used for the measurement of the elasticity modulus and the Charpy resilience coefficient.

EXAMPLE 6

The procedure according to Example 5 was repeated, but

using 975 grams of Kostil AP and 325 grams of Elaprim
AR 153.

EXAMPLE 7

The procedure according to Example 5 was repeated, but
5 using 1040 grams of Kostil AP and 260 grams of Elaprim
AR 153.

EXAMPLE 8

The procedure according to Example 5 was repeated, but
using 910 grams of Kostil AP and 390 grams of Elaprim
10 AR 152 rubber.

EXAMPLE 9 (for comparative purposes)

The procedure according to Example 8 was repeated, but
omitting the addition of zinc chloride.

EXAMPLE 10

15 The procedure according to Example 5 was repeated, but
instead of zinc chloride there were used 0.4 grams of
anhydrous cadmium chloride.

EXAMPLE 11

The procedure according to Example 5 was repeated, but
20 instead of zinc chloride there were used 0.4 g of
anhydrous ferric chloride.

In Table 3 below are given the Charpy resilience
and the elasticity modulus under bending of the
products obtained in Examples 5 to 11.

T A B L E 3

Example	Charpy resilience (kg.cm/cm ²)	Elasticity modulus under bending (kg/cm ²)
5 5	17.1	19,500
6	13.4	20,900
7	8	26,100
8	16.7	19,200
9	5.8	27,400
10 10	6.2	19,600
11	10.1	17,600

EXAMPLE 12

15 Grams of Elaprim AR 153 rubber and 35 grams of Kostil AP were mixed together in a Brabender mill running at 60 r.p.m. and with the barrel pre-heated to 170°C.

After 1 minute there were added 0.15 grams of anhydrous zinc chloride and the mixing was continued for another 5 minutes. At the end of the mixing, the temperature of the mix was about 210°C. The polymeric blend was removed from the mixer and was compression moulded into plates 1/8 inch thick that were used for measuring the Charpy resilience values and the elasticity modulus.

EXAMPLE 13

25 The same procedure was followed as in Example 12, but using 35 g of Kostil AM instead of Kostil AP.

EXAMPLE 14

The same procedure was followed as in Example 12, but using 35 grams of Kostil AF instead of Kostil AP.

The Charpy resilience and the elasticity modulus of the products obtained in Examples 12 to 14 are given in Table 4 below.

T A B L E 4

10	Example	Charpy resilience (kg.cm/cm ²)	Elasticity modulus under bending (kg/cm ²)
	12	12.6	21,000
	13	22.8	21,100
	14	17.9	21,500

EXAMPLE 15

15 91 Grams of Kostil AP, 39 g of Elaprim AR 153, and 0.4 g of anhydrous zinc chloride were mixed together in a cylinder mixer (cylinder mill) pre-heated to 170°C. After 20 minutes of mixing, the blend was discharged from the mixer and compression moulded into plates 1/8
20 inch thick. The Charpy resilience of the material tested was equal to 9.1 kg.cm/cm² while the elasticity modulus under bending was 17,500 kg/cm².

EXAMPLE 16

The procedure was followed as in Example 1, but using instead of Elaprim AR 153 rubber, a copolymer consisting of 98.5% by weight of ethylacrylate, 0.5% by weight of acrylic acid and 1% by weight of glycidyl methacrylate. The Charpy resilience of the product was 16.8 kg.cm/cm², while the elasticity modulus under bending was 19,200 kg/cm².

C L A I M S

1. A process for preparing a mix or blend of an acrylic rubber which comprises a copolymer of ethylacrylate and/or butylacrylate with acrylic and/or methacrylic acid, with a copolymer of
5 styrene with acrylonitrile, characterized by comprising mixing together the said acrylic rubber with the said styrene/acrylonitrile copolymer, at a temperature from the glass transition temperature of the styrene/acrylonitrile copolymer to
10 220°C, in the presence of from 0.05% to 2% by weight, based on the weight of the mixture of polymers, of a compound selected from zinc chloride, cadmium chloride, ferric chloride, aluminium chloride and boron trifluoride, and in
15 the presence of an epoxy cross-linking agent.
2. A process as claimed in Claim 1, characterized by the presence of zinc chloride in an amount of from 0.1% to 1% by weight based on the weight of the mixture of polymers.
- 20 3. A process as claimed in Claim 1 or 2, characterized in that the said epoxy cross-linking agent is present in an amount of 0.5 to 5 mols, based on 100 mols of acrylic rubber.